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New Separations in the Yttrium Group by Means of Stearates and Selenates

BY

CHARLES WILLIAM STODDART

Thesis Submitted for the Degree of Doctor of Philosophy
University of Wisconsin
1909

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INTRODUCTION

The separation of the rare earths has occupied the attention of chemists for more than a century, and up to the present time no perfectly satisfactory method has been discovered. The investigation here described was undertaken in the hope of finding for the yttrium group some means of separation which would be an improvement over existing methods.

C. W. S.

ACKNOWLEDGEMENT

This investigation was undertaken at the suggestion of Professor Victor Lenher, and I take this opportunity to express my deep appreciation of his advice and encouragement during the progress of the work.

C. W. S.

Chemical Laboratory
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NEW SEPARATIONS IN THE YTTRIUM GROUP BY MEANS OF STEARATES AND SELENATES

PRELIMINARY STATEMENT

The general method of separating the rare earths by fractional precipitation depends on slight differences in basicity. Any reagent which forms insoluble compounds with the earths may be used, but if the reagent in question has weak acidic or basic properties, it is of distinct advantage. When, for example, a salt of a strong base and a weak acid is added in dilute solution to a mixture of the rare earth nitrates, the strong base tends to unite first with the nitric acid radicle of the weakly basic earths, since the salt of the weak acid is readily decomposable in the presence of the stronger acid. The rare earth metal is then free to unite with the weak acid to form an insoluble compound. As the fractionation proceeds the more strongly basic earths react, and as a result a much better separation is effected than in the case of a precipitant of stronger character.

Stearic acid is a weak organic compound of the fatty series, is of high, molecular weight, and forms easily handled precipitates of the rare earths. It was therefore chosen as a reagent for attempting the fractionation of these difficultly separated elements.

The method of fractionating the earths by decomposing such salts as the nitrates or chromates by heat has been studied by Marignac,[1] Delafontaine,[2] Nilson,[3] Pattinson and Clark,[4] and many others. Since the method depends on the formation of insoluble basic salts of these elements, it is to be supposed that any salt readily decomposable by heat, will fractionate the rare earths. Selenic acid forms salts unstable towards heat and moreover from aqueous solution forms well defined, normal, crystalline salts of the rare earths; consequently the selenates of these earths were chosen to attempt a separation by fractional decomposition with heat.

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[1] Ann. de Chim. et de Phys. (3) **38**, 148; (5) **14**, 247; C. r. **87**, 578; C. r. **90**, 900.

[2] J. pr. **94**, 298, 300; C. r. **87**, 561, 933; **90**, 223; Ch. N. **75**, 229.

[3] Ber. **12**, 1, 550; **13**, 2, 1430; **15**, 2, 2526.

[4] Ch. N. **16**, 259.

In the present work the yttrium group was selected, since these earths are the most difficult to separate, and any method which effects a successful fractionation of them is of distinct merit.

STEARATE SEPARATION

Preparation of oxides.—The material employed was in the form of oxalate from monazite, the yttrium earths being separated from the cerium earths by precipitating the latter as the double potassium sulphate in a saturated solution of potassium sulphate. The cerium earths were in such excess that a considerable quantity of yttrium earths was carried down with them either by occlusion or by adsorption, although the presence of an excess of nitric acid prevented this adsorption to a very considerable extent. By treating the cerium earth double sulphates with additional water it was found possible to recover a considerable portion of the yttrium earths.

In this way several lots were obtained, amounting in all to six per cent of the original roasted oxalates. The atomic weights of the different lots varied from 117.4 to 132.2, the latter containing some didymium. It was possible to tell with considerable accuracy when the characteristic absorption bands of didymium had disappeared, by using a hand spectroscope on an eight inch layer of the filtrate from the cerium earth double sulphates.

Method of determining atomic weight.—The atomic weight determinations were made by dissolving about one gram of the oxide in nitric acid and evaporating until the excess of acid was removed. The nearly neutral nitrates were taken up with 600 cubic centimeters of water, heated to boiling, and a dilute solution of oxalic acid added drop by drop with constant stirring until all the earths were precipitated. In order that the more soluble yttrium oxalate might separate out, the precipitate was allowed to stand over night then filtered and washed with hot water until free from oxalic acid. The oxalates were dried at 105° to 125°, thoroughly mixed, and two portions of 0.2 gram each were weighed out. One portion was ignited to constant weight to obtain the percentage of earth oxide. The other portion was dissolved in dilute sulphuric acid, heated nearly to boiling, and titrated with approximately tenth normal potassium permanganate to determine the content of oxalic acid. Solving the proportion 216 : X : : per cent C_2O_3 : per cent R_2O_3, the value of R, or the atomic weight, was obtained. This procedure, devised by Walcott Gibbs, is a satisfactory method for determining the molecular weight of the rare earth.

Preparation of potassium stearate. — For the first fractionations there was used pure stearic acid whose melting point was very close to 69°. Later it was found that commercial stearic acid with a melting point of 55° was just as satisfactory. This material was a mixture of approximately 50 per cent stearic acid and 50 per cent palmitic and oleic acids. Since the commercial acid is very much cheaper, and yet just as effective, its use is of great advantage.

In the beginning of the experiments an aqueous solution of potassium stearate was prepared by heating together in a pressure flask stearic acid and potassium hydroxide with sufficient water to form a thick paste. The stearic acid was always in slight excess of the amount necessary to form a neutral salt. Although considerably diluted before use the liquid was viscous even when warm. An alcoholic solution of potassium stearate was found more satisfactory, since it gave a clear mobile liquid when warm. This was preferably of 50 per cent strength, for the stearate in dilute alcohol solidifies at a lower temperature than in stronger alcohol, thus necessitating less heating of the precipitant during its addition to the material to be fractionated. The solution of alcoholic potassium stearate was prepared by dissolving the stearic acid in 95 per cent alcohol, adding potassium hydroxide to slight alkalinity with phenolphthalein, and discharging the color with more stearic acid. Sufficient water was then added to make a 50 per cent solution. The dilution employed in all the experiments was 0.2 gram of stearic acid per cubic centimeter.

Methods of fractionation. — In all cases the oxides of the rare earths were dissolved in nitric acid, and the excess of acid removed by evaporation. The sirupy residue was taken up with water and diluted to a volume of at least 500 cubic centimeters.

It was found that if the stearate was added rapidly the precipitate was hard and lumpy and the separation poor, due to the occurrence of complete local precipitation where an excess of stearate came in contact with the rare earth nitrates. But if the stearate was added drop by drop, and the solution stirred violently the precipitate was loose, fine grained, easily washed, and the separation excellent.

Stirring was accomplished in various ways. Using a glass rod and stirring by hand was hardly sufficient. Shaking the solution in a flask could not be carried on while the precipitant was being added, and agitation at this time is preferable. Boiling the solution violently caused the precipitate to melt, and when cold to form a solid crust on the liquid.

The method finally adopted was to add drop by drop from a burette a 50 per cent alcoholic solution of potassium stearate to a cold solution of earth nitrates diluted to 2,000 cubic centimeters. The solution was contained in a large bottle or decanting jar and agitated by a glass stirrer, driven at a speed of about 1,200 revolutions per minute by a small electric motor. The stirring was continued several minutes after the addition of the precipitant. By using a Büchner funnel with two or three thicknesses of filter paper, it was possible to wash the precipitate very rapidly, after which it was ignited to the oxide. The filtrate was evaporated down to 2,000 cubic centimeters and cooled before adding the next portion of stearate.

The first fraction removed was always smaller in amount than the succeeding ones, and the precipitate had a tendency to be hard and lumpy. This was due to the liberation of free stearic acid by the slight excess of nitric acid in the rare earth solution.

The use of the mechanical stirrer changed the character of the precipitate from a coarse texture of curdy consistency to a fine grained, soft, very light material. In one instance where the stirring was continued over night, the floating precipitate dried on the top to a feathery mass which was so light that it was ejected from the jar to a considerable distance.

Separations effected.—The first fractionation was made on 10 grams of yttrium earth oxide with an atomic weight of 118.1. Nineteen fractions were removed by adding various amounts of the aqueous solution of potassium stearate. Table I gives the atomic weights of the fractions.

TABLE I.

Atomic weights of the first series of fractions.

Number of fraction.	Atomic weight.	Number of fraction.	Atomic weight.
1	124.5	11	120.7
2	127.0	12	123.1
3	129.2	13	121.6
4	119.7	14	118.9
5	125.4	15	118.9
6	125.3	16	113.3
7	123.3	17	107.9
8	123.3	18	102.7
9	124.4	19	103.7
10	120.5		

The atomic weights do not diminish regularly from first to last, due in great measure to the changes in methods of fractionation. The precipitate in many instances was not homogeneous, owing to complete local precipitation having taken place where the precipitant was added too rapidly. Apparently such a large number of fractions is unnecessary, but the fact is clearly brought out that the stearate method is able to separate the rare earth oxides of atomic weight 118.1, into fractions varying from 129.2 to 102.7.

The second fractionation was carried out on 10 grams of earth oxide with an atomic weight of 117.4, using a solution of potassium stearate in 95 per cent alcohol, and adding it drop by drop from a burette, it being necessary to warm the burette from time to time with a Bunsen burner to keep the solution liquid. After the addition of the precipitant the mixture was shaken violently in a flask. Six fractions were removed, the atomic weight of each being as follows: 122.8, 119.8, 116.8, 115.6, 106.7, 103.7. From these results it is to be noted that approximately the same degree of separation may be effected in six fractions as in nineteen, if the conditions are slightly changed.

In order to try the method on a larger scale, 50 grams of rare earth oxides of atomic weight 118.1 were dissolved in nitric acid and fractionated with alcoholic potassium stearate. Each part of the first series was fractionated again and suitable fractions combined. In this way sixteen fractions were obtained and united, according to their atomic weights, into four portions, the atomic weights of each being 123, 120, 114, and 112.

The separation effected here was not particularly good. Sufficient time had not been allowed for equilibrium to be established, as will be discussed later. The precipitate, moreover, was in many cases so coarse that some of the solution was occluded. From this point, however, the fractions were obtained by the use of the stirrer and the 50 per cent alcoholic solution of potassium stearate. It was found that instead of obtaining fractions of equal weight, if several small fractions were first removed, the heavier earths could be separated more rapidly and a large fraction left with materially lighter atomic weight. For example, with 10 grams of oxide there were removed four fractions of 1.5 grams each, and one fraction of 4 grams.

With these improvements in method, the four portions mentioned above, having atomic weights of 123, 120, 114, and 112, were separated into numerous fractions, the various fractions in the different groups united according to the color of the ignited stearates and refractionated. The colors varied from dark brown to light yellow or buff. Thirty-three fractions were thus obtained. Three were united whose color was almost white and whose atomic weight was 92. This lot was separated into four fractions, the last one having an atomic weight of 90.6, and was practically pure yttrium. The quantity, however, was so small that further fractionation was impossible, although there is no doubt that yttrium of atomic weight 89 could be obtained very easily from this material.

Absorption spectra.— Twenty-nine of the thirty-three fractions in the last series were examined for absorption bands by means of a Steinheil grating spectroscope with vernier attachment for reading degrees of arc. A simple logarithmic calculation gave the wave lengths of the absorption bands. Nitric acid solutions were used containing 10 per cent of the earth oxide. The layer of solution examined was 17.5 mm. thick.

It is unnecessary to give the wave lengths for each fraction since there was very slight variation in many cases. Table II gives the wave lengths for the first fraction and for the twenty-ninth fraction, whose atomic weight was 101.4. In comparison there is given the spectrum of a sample of erbium nitrate prepared from monazite by Dr. Waldron Shapleigh.

TABLE II.

Absorption spectra of the first stearate fraction, of the twenty-ninth stearate fraction, and of erbium nitrate (Shapleigh's).

FIRST FRACTION.		TWENTY-NINTH FRACTION.		ERBIUM NITRATE.	
Wave Length.	Strength.	Wave length.	Strength.	Wave length.	Strength.
....	....	444.2	very faint	....	....
....	....	....	....	452.0	very faint
458.0	fairly strong	462.3	very faint	457.4	fairly strong
463.7				464.1	very faint
493.7	very faint	495.1	very faint	493.5	very faint
496.4	fairly strong			496.8	fairly strong
529.1	very faint	529.4	haze	527.6	very faint
543.7	strong	532.6	fairly strong	533.0	strong
544.7	fairly strong	545.3	faint	545.6	faint
....	....	....	....	550.5	very faint
580.2	faint	579.2	faint	579.5	fairly strong
589.9		590.9		590.2	
647.5	fairly strong	648.4	faint	649.3	faint
651.1					
....	....	....	....	657.3	very faint
661.7	fairly strong	664.3	very faint	661.7	faint

Examining the table it may be seen that most of the lines are those of erbium, or at least of earths very closely associated with erbium, such as samarium, holmium, and europium. The lines fade markedly as the fractionation progresses, but persist throughout the series until there is obtained the last fraction which had an atomic weight of 90.6. This portion gave absolutely no absorption spectrum.

STEARATE SEPARATION OF YTTRIUM EARTHS FROM GADOLINITE

To test the separation of the yttrium earths from gadolinite, about eight grams of oxide, freed from the cerium group by precipitation of the latter with potassium sulphate, were separated into five fractions. The first fraction had an atomic weight of 109.6, the last fraction of 97.4. This material contained a higher percentage of yttrium than did the monazite earths, and the progress of the fractionation indicated a rapid approach to the separation of this element from its companions.

For the purpose of obtaining a homogeneous precipitate of the stearates and of effecting better separation, it is important: First, to add a dilute solution of potassium stearate to a dilute solution of the rare earth nitrates; second, to add the precipitate drop by drop; and third, to stir the solution while adding the precipitant. These conditions also favor the establishment of equilibrium in the system between that portion which is precipitated and that which remains in solution. If a strong solution of potassium stearate should be added to a strong solution of the earths, and the mixture not stirred, there would be complete local precipitation and not fractional precipitation.

There is another factor entering into the more complete separation of these earths, namely: Time. In other words, if the mixture of precipitate and solution is stirred for a considerable period, a secondary decomposition takes place, which markedly changes the chemical composition of the precipitate. This fact was very plainly shown in an experiment conducted as follows:

Seven-tenths of a gram of an oxide whose element had an atomic weight of 109.6 was dissolved in nitric acid, evaporated, and taken up with water to a bulk of 2000 cubic centimeters. To this was added the thoroughly washed precipitate of earth stearates from seven-tenths of a gram of an oxide whose element had an atomic weight of 97.4. This mixture was stirred for about twelve hours. At the end of this time the precipitate had changed physically from a coarse, soft, curdy consistency, to a very fine grained, light, fluffy mass. The precipitate was filtered, washed thoroughly, and the atomic weight of its element found to be 102.8. This increase in atomic weight from 97.4 to 102.8 showed that a very decided secondary decomposition had taken place between the solid stearate and the liquid nitrate.

Ideal conditions for fractionation are very dilute solutions of earth nitrate and of potassium stearate, slow addition of the precipitant, and stirring for at least twelve hours. If these conditions, more particularly the very long stirring, are fulfilled, a cleaner separation results, and pure yttrium is obtained much more rapidly. The strong base, yttrium, has the greatest attraction for the strong acid, nitric, and as long as there are weaker bases in solution, and as long as the stearic acid is not in excess, the weaker bases are thrown out first, if equilibrium is allowed to take place.

BEHAVIOR OF YTTRIUM EARTH STEARATES TOWARDS ANHYDROUS SOLVENTS

In order to test the solubility of the stearates of the rare earths in anhydrous compounds and subsequently to investigate the ability of the latter to extract them differentially, a portion of earth oxide of atomic weight 118.1 was dissolved in nitric acid, evaporated to a thick sirup, diluted with water, and all the rare earths precipitated by potassium stearate. The precipitate was filtered, washed, dried, and pulverized.

A part of this substance was placed in a Schleicher and Schüll paper thimble in a Soxhlet extractor and subjected to extraction with *ether* for some time. Only stearic acid was removed. This was present in the original mass in the free state, having been liberated from the potassium salt by the excess of nitric acid in the original solution.

Benzene extracted a portion of the rare earths. A determination of the atomic weight of the extracted material gave 116.6, of the part remaining in the thimble, 117.5.

Carbon tetrachloride extracted a portion which gave an atomic weight of 116.9. The fraction remaining behind was 117.4 in atomic weight. Further treatment extracted practically all of the rare earth stearates.

Carbon disulphide extracted nothing but stearic acid.

Alcohol extracted only stearic acid.

Xylene extracted a portion whose atomic weight was 117.8. All of the material was soluble finally.

Toluene dissolved all of the material.

Chloroform extracted only stearic acid.

Melted *naphthalene* and *anthracene* dissolved all of the material, as did hot *olive oil*.

From these results it can be seen that the yttrium earth stearates are soluble in anhydrous compounds of relatively high boiling points, but there is no one rare earth stearate markedly different in solubility from the rest.

FRACTIONAL DECOMPOSITION OF YTTRIUM EARTH SELENATES BY HEAT

Heating yttrium earth selenates alone.— Following the analogy of the basic nitrate method, the yttrium earth selenates were fractionally decomposed by heat. Selenic acid was prepared by the method of treating silver selenite with bromine and filtering off the silver bromide. The filtrate was evaporated to a thick sirup, each cubic centimeter of which contained approximately 0.5 gram of selenic acid. A portion of earth oxide was converted to selenates by dissolving in a slight excess of selenic acid, evaporating down almost to dryness and filtering off from the excess of acid. The pink crystalline residue was dried and pulverized.

A fairly satisfactory method of observing the temperature of decomposition, and at the same time of collecting the fumes of selenium dioxide, was to place the selenates in a hard glass test tube with a side tube fused in near the top. A thermometer registering up to 550° was inserted in the mass and fitted into the tube by a ring of asbestos paper. The side tube was connected through wash bottles to a suction pump and a stream of air drawn through the apparatus, the asbestos stopper not being air tight. The tube containing the selenate was fitted into a second larger hard glass test tube with an asbestos stopper. This formed an air jacket around the tube containing the selenates, and insured a uniform heating of the mass.

As the material was slowly heated, water of crystallization began to come off, then light fumes of selenium dioxide, followed by a more or less copious evolution of the latter. It was impossible to note the beginning of decomposition, but it was approximately 330°, although in one case the fumes of selenium dioxide were noticed at 290°. The mass did not melt up to 500°.

After heating above 300°—part of the time as high as 400° or 450°—for about an hour, the apparatus was allowed to cool, the mass emptied into a casserole, and water added. The dry material hydrated violently, considerable heat being generated. After heating on a hot plate for a few minutes the yellowish white, granular to flocculent residue was filtered off and washed, the filtrate evaporated to dryness, pulverized, and again decomposed. After washing out the soluble selenates and dissolving in hydrochloric acid to reduce the selenates to selenites, the residue showed the presence of selenium when treated with sulphur dioxide. The mass was a basic selenate. Four fractions were obtained from twenty-five grams of selenate. The residue for atomic weight determinations was dissolved in nitric acid, evaporated nearly to dryness to expel the excess of acid, taken up with water, and oxalic acid added. The oxalates were washed until free from selenium and ignited. The atomic weight of the original material was 112. The first fraction had an atomic weight of 120.4 and the fourth fraction, 104.9.

Another lot of forty grams of the rare earth selenates were fractionated five times by heat and appropriate fractions were united. The united portion was decomposed as before into six fractions. The last fraction had an atomic weight of 103.1.

Table III gives the spectra of the original material and of the last fraction.

TABLE III.

Absorption spectra of original material and of last fraction in the selenate separation.

ORIGINAL MATERIAL.		LAST FRACTION.	
Wave length.	Strength.	Wave length.	Strength.
452.0	faint	....	....
457.1 463.2	fairly strong	458.7 462.9	fairly strong
493.3	very faint	492.3	very faint
496.8	fairly strong	495.9	fairly strong
500.9	faint	....	....
528.5	very faint	528.5	very faint
532.6	strong	531.7	strong
545.2	fairly strong	545.6	fairly strong
551.4	faint	550.5	faint
581.3 591.5	faint	....	....
649.3	faint	648.8	faint
657.3	faint	....	....
661.4	fairly strong	661.0	fairly strong
675.0	faint	....	....

By comparing the spectrum of the last selenate fraction with the spectrum of the last fraction of the stearate separation (Table II) it is to be noted that the lines, although stronger, are fairly similar in wave length, showing principally erbium bands. The atomic weight of the selenate fraction is greater than that of the stearate fraction, 103.1 to 101.4. Compared to the original material, the last selenate fraction shows bands of equal strength but much fewer in number.

Heating yttrium earth selenates with potassium selenate.— The basic nitrate method consists in heating the earth nitrates alone. Debray[1] modified the original method by melting the nitrates of the earths with nitrate of potassium. Schützenberger and Boudouard[2] used a mixture of potassium and sodium nitrates with the rare earth nitrates. The mass melts before decomposition begins.

Following the analogy of these modifications, the rare earth selenates were mixed with an equal amount of potassium selenate—25 grams of each—and heated in an apparatus similar to that described above for the earth selenates alone. The decomposition was similar to that of the earth selenates heated alone, except that the evolution of selenium dioxide was much more copious, subliming in all the cooler parts of the apparatus, and even stopping up the exit tube. The mixture did not melt up to 500°. In the same length of time less rare earths were rendered insoluble than when the earth selenates were heated alone. Five fractions were obtained, the first with an atomic weight of 117.8 and the fifth of 109.1.

DISCUSSION OF RESULTS

In the year 1896 Drossbach[3] obtained by fractional precipitation with sodium hydroxide, and also by fractional crystallization of the sulphates, a white oxide whose element had an atomic weight of approximately 100. Also in 1896 Schützenberger and Boudouard,[2] by alternating the basic nitrate method with fractional crystallization of the sulphates, obtained a white oxide whose atomic weight was 102. Since these investigators were unable to further decompose this fraction, they assumed that they had an element whose atomic weight was approximately

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[1] C. r. **96**, 828.

[2] C. r. **122**, 697.

[3] Ber. **29**, 3, 2452.

100. In 1897, Urbain and Boudischovsky[1] by using the acetylacetonate method obtained several fractions whose atomic weights averaged about 100.

In 1900, however, Urbain[2] was able to carry the fractionation further with the ethyl-sulphate method, obtaining two portions whose atomic weight was 152 on one hand, and pure yttrium on the other. He claimed that the product obtained by Drossbach, Schützenberger and Boudouard, as well as by himself previously, was a mixture of pure yttrium and the terbium earths. In all the above cases the material employed was from monazite.

Referring back to the last fractions of the first two series by the stearate separation on page 5, it will be noticed that the atomic weights were 103.7 in both cases, also that in the two series obtained by decomposition of the rare earth selenates the final fractions had atomic weights of 104.9 and 103.1. Undoubtedly these are the same fractions obtained by the investigators above mentioned. It is to be observed that this fraction of approximately 102 is obtained only from monazite yttrium earths. In the stearate separation on the gadolinite earths no such fraction was obtained.

The earths of the yttrium group are characterized by such a similarity one with another, that by any method their separation is difficult. In the case of the yttrium earths from monazite, however, this difficulty of separation apparently reaches a climax when the mixture has an atomic weight of approximately 102. This particular fraction was so difficult of separation that as seen above, some of the previous investigators went so far as to think that they had obtained a new element. The later work of Urbain, however, dispelled their illusion.

It is customary in preparing pure yttrium to use alternately various methods, since most reagents are unable to carry the separation beyond a certain point. A different reagent is necessary to effect a further separation. The fraction from monazite earths having an atomic weight of 102 presents more than ordinary difficulties of separation, even when the methods are changed. It is to be noted, however, that the use of potassium stearate as a reagent is in itself sufficient to carry the fractionation from the original material down to pure yttrium without using any other reagent. It is true that there is a momentary pause at the fraction of atomic weight 102, indicating a combination whose separation causes more than ordinary difficulty.

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[1] C. r. **124**, 618.

[2] Ann. de Chim. et de Phys. **19**, 184.

In explaining the difficulty of separating the fraction whose atomic weight is 102, two possibilities suggest themselves:

First, that there is a new element in monazite very closely allied with yttrium and so near like it in its properties that it is very difficult to separate them. In passing Crookes' victorium[1] might be mentioned. This element, which Crookes claims to have separated from samarskite, gadolinite, cerite, and other similar minerals, has an atomic weight of approximately 118, and is very like yttrium in properties. The presence of a new element, however, has been disproved by the work of Urbain, mentioned above.

Second, that there is formed a pseudo-compound of yttrium with other members of the group—a compound which gives an atomic weight of 103 for the element. The average atomic weight of the other members of the group is 166 and calculating with this average figure it would mean a compound of four parts yttrium to one part of the other members of the group.

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[1] Chem. N. **80**, 49.

CONCLUSIONS

1. The fractional decomposition of the yttrium earths by heating their selenates offers a method of separation in every way as satisfactory as the well known basic nitrate method. In very few fractions widely divergent atomic weights are obtained, and marked changes in absorption bands are effected. With improved apparatus for regulating the heat and for handling the products of decomposition, still better results could be obtained.

2. Heating the earth selenates with potassium selenate offers no advantage over the heating of the earth selenates alone.

3. The stearate method is of distinct advantage over existing methods in many ways. The precipitate formed is easily filtered and washed, the precipitant cheap, the separations sharp and distinct. For the preparation of pure yttrium from monazite it is decidedly the best method known, and yttrium is one of the most difficult rare earths to separate pure. Only one reagent is necessary, and few fractionations required, thereby saving a great amount of time, as well as of material, in a large number of manipulations. There is a brief pause in the progress of the fractionation at the portion which has an atomic weight of approximately 102.

4. The stearate method applied to the yttrium earths from gadolinite effects a rapid separation without the pause at the fraction having an atomic weight of 102.

5. Yttrium earth stearates are soluble in anhydrous compounds of relatively high boiling point, but they are not extracted differentially from such solvents.

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